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Synthesis, Characterization, and Catalytic Applications of Palladacyclic Complexes Bearing C,N,S-Donor Ligands

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The preparations of novel tridentate C,N,S-donor ligand precursors, PhN=C(CMe$_2$)(NPh)C=N(CH$_2$)$_2$SR [R = CMe$_3$ (**2**); R = Ph (**3**)] are described. Treatment of **2** and **3** with 1 equiv. of Pd(OAc)$_2$ affords the orthometallated palladium(II) complexes [PhN=C(CMe$_2$)(N-η^1-Ph)C=N(CH$_2$)$_2$SR]Pd(OAc) [R = CMe$_3$ (**4**); R = Ph (**5**)]. Reaction of **4** and **5** with an excess of LiCl in methanol affords the orthometallated palladium(II) complexes [PhN=C(CMe$_2$)(N-η^1-Ph)C=N(CH$_2$)$_2$SR]PdCl [R = CMe$_3$ (**6**); R = Ph (**7**)]. Crystal structures are reported for compounds **3** and **4**. The application of these novel palladacyclic complexes as catalyses for the Suzuki and Heck reactions with aryl halide substrates was examined.

Introduction

Due to the powerful application of, and versatile methods for, the formation of carbon-carbon bonds, palladium-catalyzed coupling reactions have been an attractive area of research.[1–19] Among these studies, the search for appropriate ancillary ligands that can serve as catalyst precursors is of current interest. Palladacycles bearing a metallated carbon atom and dative group(s) are the most active catalyst precursors for the promotion of such reactions.[2–8,11–17,19] These complexes are usually formed as dinuclear species with bridged ligands, or as mononuclear species in the presence of ligands with neutral dative groups. In order to improve the stability and efficiency of catalytic palladium complexes, various families of palladium based catalyst precursors have been developed. Recently, some sulfur containing palladacycles that function as excellent catalyst precursors for coupling reactions have been reported. [20–30] Their success in catalyzing cross-coupling reactions encouraged us to study the catalytic performance exhibited by palladacycles with pendant thioether functionalities. Following our previous work on four-membered ring diimino palladacycles,[31] we report here the synthesis and characterization of novel mononuclear palladacycles incorporating unsymmetrical C,N,S-donor ligands. Their catalytic activities toward the Suzuki and Heck reactions were investigated.

Results and Discussion

Syntheses and Characterization of Ligand Precursors and Palladacycles

Pre-ligand compound **1** was prepared by the reaction of 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride with 3.0 equiv. of 2-chloroethylamine hydrochloride in the presence of 4.0 equiv. of NEt$_3$ using a similar procedure to that reported in the literature.[31] The new ligand precursors **2** and **3** were synthesized from **1** via a nucleophilic substitution reaction with the corresponding thiol [R = C(CH$_3$)$_3$ for **2**; R = Ph for **3**].[20] Compounds **1**, **2**, and **3** were characterized by NMR spectroscopy and elemental analysis, which indicated that they are four-membered ring diimine compounds with the different functionalities. A summary of the synthetic route and the proposed structures is shown in Scheme 1. The X-ray structure of **3** features a four-membered diimine ring bearing a pendant thioether functional group. The molecular structure is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The C(1)–N(1) [1.253(2) Å] and C(3)–N(3) [1.257(2) Å] bond lengths are consistent with these bonds possessing significant double bond character, and the bond angles around the imino C and N atoms are indicative of sp^2 hybridized centers.

Treatment of **2** and **3** with 1 equiv. of Pd(OAc)$_2$ at room temperature yields complexes **4** and **5**, respectively, as pale brown solids. Similar to the results reported previously,[31] an additional tertiary carbon was found in the phenyl ring region of the ^{13}C{^{1}H} NMR spectrum that indicates the presence of a metallated carbon atom, which was created during the reactions. Crystals of **4** suitable for structural determination were obtained from a CH$_2$Cl$_2$/hexane solu-

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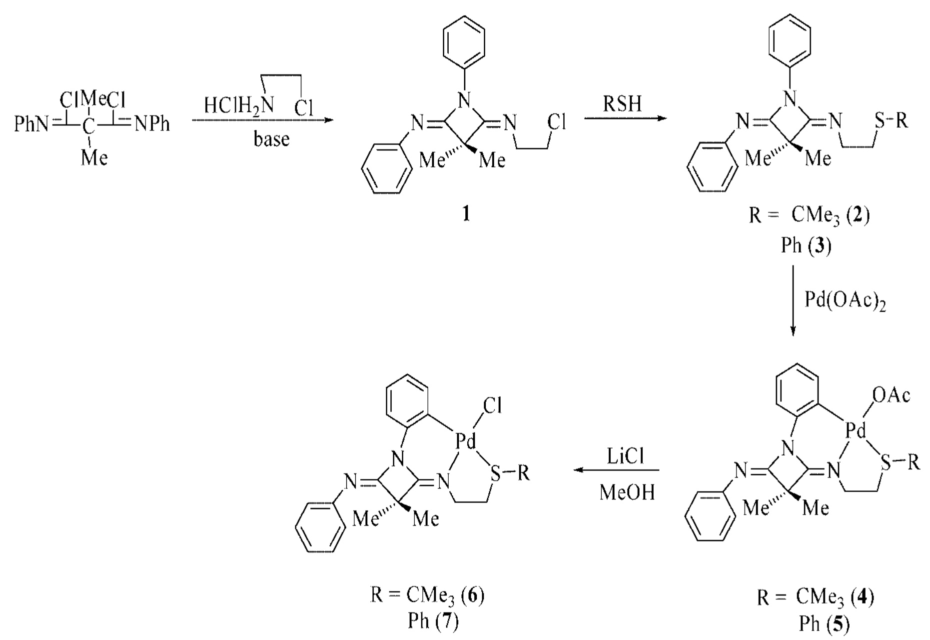


Scheme 1.

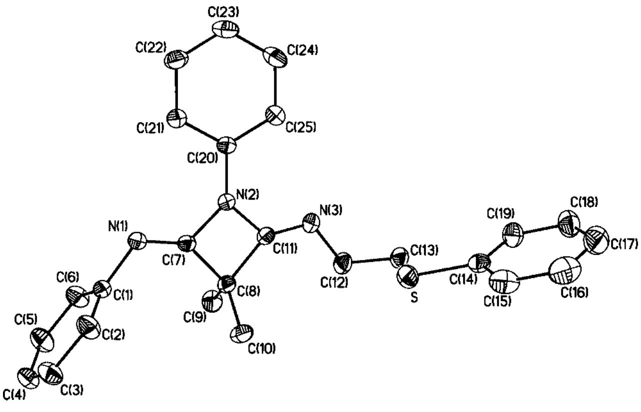


Figure 1. Molecular structure of compound **3**. Hydrogen atoms bound to carbon atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **3**.

S–C(14)	1.751(2)	S–C(13)	1.789(2)
N(1)–C(7)	1.252(2)	N(1)–C(1)	1.427(2)
N(2)–C(7)	1.403(2)	N(2)–C(11)	1.411(2)
N(2)–C(20)	1.413(2)	N(3)–C(11)	1.251(2)
N(3)–C(12)	1.467(3)		
C(14)–S–C(13)	104.20(10)	C(7)–N(1)–C(1)	119.15(15)
C(7)–N(2)–C(11)	93.61(13)	C(7)–N(2)–C(20)	133.05(15)
C(11)–N(2)–C(20)	133.33(16)	C(11)–N(3)–C(12)	118.34(17)
N(1)–C(7)–N(2)	128.08(16)	N(1)–C(7)–C(8)	140.33(17)
N(2)–C(7)–C(8)	91.58(14)	C(7)–C(8)–C(11)	83.57(13)
N(3)–C(11)–N(2)	127.21(17)	N(3)–C(11)–C(8)	141.54(17)
N(2)–C(11)–C(8)	91.22(14)		

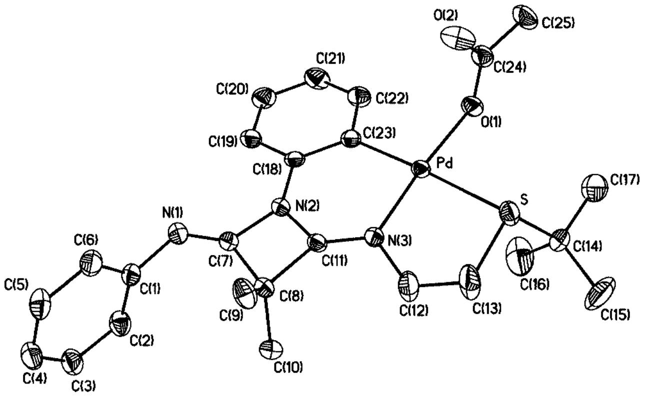


Figure 2. Molecular structure of complex **4**. Hydrogen atoms bound to carbon atoms have been omitted for clarity. Dichloromethane and water molecules are omitted for clarity.

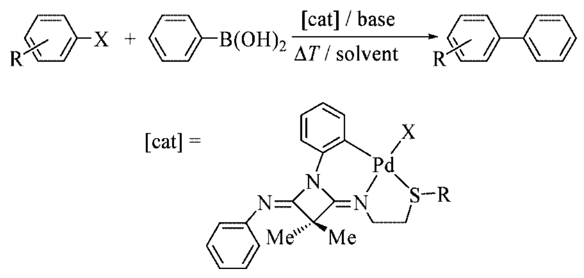
Table 2. Selected bond lengths [Å] and angles [°] for **4**.

Pd–N(3)	2.011(3)	Pd–C(23)	2.022(4)
Pd–O(1)	2.036(2)	Pd–S	2.4093(9)
N(3)–Pd–C(23)	93.47(12)	N(3)–Pd–O(1)	174.95(11)
C(23)–Pd–O(1)	91.47(13)	N(3)–Pd–S	84.62(8)
C(23)–Pd–S	176.85(11)	O(1)–Pd–S	90.40(8)

tion. The molecular structure is shown in Figure 2, and selected bond lengths and angles are listed in Table 2. The bond angles [in the range of 84.62(8) to 93.47(12)°] around the palladium metal center indicate that the complex has a slightly distorted square planar geometry, in which the palladium metal center is coordinated to one imine nitrogen atom, one thioether sulfur atom, one carbon atom, and one OAc oxygen atom. The N–Pd–$C_{metallated}$ bite angle [93.47(12)°] involving the imino nitrogen and metallated carbon atoms is similar to those [93.20(104)°, 93.77(8)°, and 94.51(10)°] found in our previous work.[31] The N–Pd–S bite angle [84.62(8)°] involving the imino nitrogen atom and the pendant group is in the range [84.46(10)–85.1(1)°] found for C,N,S-donor complexes with two carbon spacer atoms between the nitrogen and sulfur atoms.[32–34] The Pd–S bond length [2.4093(9) Å] is in the range [2.240(1)–2.422(1) Å] found for palladium complexes containing thioether functionalities.[23,25,30,32–37] The Pd–$C_{metallated}$ bond length [2.022(4) Å] is in the range [1.964(3)–2.034(2) Å] found for palladacycles with metallated carbon.[23,31–34,38] The Pd–$N_{C=N}$ bond length [2.011(3) Å] is within the range [1.985(3)–2.098(2) Å] found for palladacycles.[31–34,38] The Pd–O_{OAc} bond length [2.036(2) Å] is comparable to those [2.0027(9)–2.105(2) Å] found in the literature.[31,39–41] The reaction of **4** and **5** with an excess of lithium chloride, in methanol at room temperature, yielded complexes **6** and **7**, respectively, as yellow solids.[42] Compounds **6** and **7** were characterized by NMR spectroscopy and elemental analysis. Basically, **6** and **7** are quite similar to **4** and **5**, but with Cl coordinated to the metal centre instead of an OAc group.

Catalytic Studies

Due to the success of some sulfur containing palladacycles in catalyzing cross-coupling reactions,[20–30] the palladacycles discussed above are expected to catalyze carbon-carbon coupling reactions. For the purpose of comparing the reactivity of complexes **4**–**7** with other palladacycles, the Suzuki reaction was chosen to demonstrate the catalytic activities of these sulfur containing complexes, as shown in Scheme 2. The potential catalyst precursor candidates **4**–**7** were investigated in the coupling of 4-bromoacetophenone with phenylboronic acid at 50 °C, over a period of 1 h on a 1 mol-% scale. Selected results are listed in Table 3. The optimum conditions for the reaction were found to be K_3PO_4/toluene, Cs_2CO_3/DMA, and Cs_2CO_3/DMF for **4** (entries 1–3); K_3PO_4/DMF for **5** (entry 4); Cs_2CO_3/THF, Cs_2CO_3/toluene, and Cs_2CO_3/DMA for **6** (entries 5–7); Cs_2CO_3/THF for **7** (entry 8). Higher reactivity was observed, under optimum conditions, for palladacycles containing a pendant *t*BuS moiety. Moreover, compounds containing an acetate group demonstrated slightly higher catalytic activities than those containing a Cl group.



Scheme 2. Application of the palladacycles in the Suzuki reaction.

Although both sets of optimized conditions, K_3PO_4/toluene and Cs_2CO_3/DMF, for **4** exhibited similar conversion levels with electronically activated aryl bromide (entries 1–2 and 9–12), poor conversion levels were observed for reactions with electronically deactivated compounds using Cs_2CO_3/DMF (entries 14–15 and 17–18). Therefore the op-

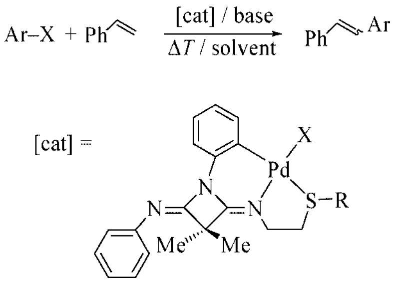
Table 3. Suzuki coupling reactions catalysed by the new palladium complexes.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol-%)	T [°C]	t [h]	Conversion (%)[b]	Yield (%)[c]
1	**4**	4-bromoacetophenone	K_3PO_4	toluene	1	50	1	96	90
2	**4**	4-bromoacetophenone	Cs_2CO_3	DMF	1	50	1	98	92
3	**4**	4-bromoacetophenone	Cs_2CO_3	DMA	1	50	1	94	83
4	**5**	4-bromoacetophenone	K_3PO_4	DMF	1	50	1	92	85
5	**6**	4-bromoacetophenone	Cs_2CO_3	THF	1	50	1	87	82
6	**6**	4-bromoacetophenone	Cs_2CO_3	toluene	1	50	1	90	88
7	**6**	4-bromoacetophenone	Cs_2CO_3	DMA	1	50	1	88	85
8	**7**	4-bromoacetophenone	Cs_2CO_3	THF	1	50	1	87	76
9	**4**	4-bromobenzaldehyde	K_3PO_4	toluene	1	50	1	99	92
10	**4**	methyl 4-bromobenzoate	K_3PO_4	toluene	1	50	1	99	95
11	**4**	4-bromobenzaldehyde	Cs_2CO_3	DMF	1	50	1	96	90
12	**4**	methyl 4-bromobenzoate	Cs_2CO_3	DMF	1	50	1	99	94
13	**4**	4-bromotoluene	K_3PO_4	toluene	1	110	0.75	99	90
14	**4**	4-*tert*-butylbromobenzene	K_3PO_4	toluene	1	70	3.5	92	86
15	**4**	4-bromoanisole	K_3PO_4	toluene	1	70	4	97	90
16	**4**	4-bromotoluene	Cs_2CO_3	DMF	1	135	0.75	99	89
17	**4**	4-*tert*-butyl-bromobenzene	Cs_2CO_3	DMF	1	70	3.5	83	75
18	**4**	4-bromoanisole	Cs_2CO_3	DMF	1	70	4	83	76
19	**4**	4-bromoacetophenone	K_3PO_4	toluene	0.01	80	2.5	87	81
20	**4**	4-bromoacetophenone	K_3PO_4	toluene	0.002	80	5	99	96
21	**4**	4-chloroacetophenone	K_3PO_4	toluene	1	80	4	9	–
22	**4**	4-chloroacetophenone	Cs_2CO_3	DMF	1	80	4	85	80
23	**4**	methyl 4-chlorobenzoate	Cs_2CO_3	DMF	1	80	4	72	70
24	**4**	4-chloroanisole	Cs_2CO_3	DMF	1	80	7	82	75
25	**4**	4-chloroacetophenone	Cs_2CO_3	DMF	1	135	4	92	90

[a] Reaction conditions: 1.0 mmol aryl halide, 1.5 mmol phenylboronic acid, 2.0 mmol base, 2 mL solvent. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield (average of two experiments).

timized conditions, K_3PO_4/toluene, were chosen for use in further studies to examine the limitations of the catalytic capability of compound **4**. Due to the high reactivity of **4**, lower catalyst concentrations were required, catalyst/substrate ratios from 10^{-4} to 2×10^{-5} were employed, leading to turnover numbers of up to 48000 within a 5 h period (entries 19–20). Similar conditions were applied during the reaction of the electronically activated aryl chloride with 1 mol-% catalyst loading; however, poor conversion levels were observed after 4 h (entry 21). Surprisingly, the percentage conversion increased to 85% after 4 h (entry 22) using Cs_2CO_3/DMF. These conditions were employed in a reaction using methyl 4-chlorobenzoate and resulted in percentage conversion levels of up to 72% within 4 h (entry 23). A similar conversion level was observed using electronically deactivated aryl chloride and 4-chloroanisole as substrates; however, the reaction took up to 7 h (entry 24). In order to compare the catalytic activities with the sulfur containing palladacycles,[22] the optimized conditions at 110 °C and 135 °C were employed in the reaction with 4-bromotoluene as the substrate, this gave conversion levels of up to 99% within 0.75 h (entries 13 and 16). A similar conversion level was observed using electronically activated aryl chloride and 4-chloroacetophenone as the substrates; however, the reaction took up to 4 h at 135 °C (entry 25).

In order to determine the influence of the pendant functionality on the catalytic activity,[21] compounds **4**–**7** were investigated as catalysts in the Heck coupling reaction of 4-bromoacetophenone with styrene at 135 °C over a period of 1.5 h on a 1 mol-% scale, as shown in Scheme 3. Selected results are listed in Table 4. The optimum conditions were found to be Cs_2CO_3/DMF for **4** (entry 1); KF/DMA for **5** (entry 2); K_3PO_4/DMA for **6** (entry 3); KF/DMA for **7** (entry 4). High reactivity was observed for **4** under optimized conditions. A similar conversion level was observed using methyl 4-bromobenzoate as the substrate (entry 5). Similar conditions were applied to the reactions employing the electronically deactivated aryl bromide compounds; however, the reactions took up to 6 h (4-bromotoluene) and 12 h (4-bromoanisole) at 135 °C (entries 6 and 7). Lower catalyst concentrations, catalyst/substrate ratios of 10^{-3} to 10^{-5}, led to percentage conversion levels of 81% after 6 h and 21% after 24 h (entries 8 and 9). Compound **4** also showed catalytic activity for reactions involving both electronically activated and deactivated aryl chlorides; however, higher catalyst loadings were necessary (entries 10 and 11).



Scheme 3. Application of the palladacycles in the Heck reaction.

Summary

Mononuclear phosphane-free palladacycles have been prepared using tridentate ligands containing carbon, nitrogen, and sulfur. Under optimized conditions, palladacycle **4** exhibits catalytic activity comparable to existing sulfur containing palladacyclic systems employed in the Suzuki coupling reaction. Complex **4** exhibits higher catalytic activity in some cases than in others. The catalyst productivity for the coupling of an electronically activated aryl bromide with phenylboronic acid was observed with a turnover of up to 48000 during a 5 h period. Complex **4** also demonstrates catalytic activity with less reactive aryl chlorides containing both electron withdrawing and electron donating groups. In the case of the four-membered diimine palladacyclic system, the thioether containing palladacycle exhibits better catalytic activity for the Heck coupling reaction than the nitrogen containing palladacycles reported in our previous work. Studies relating to the fine-tuning of the ligands, and investigations into further catalytic applications for metal complexes are currently underway.

Table 4. Heck coupling reactions catalysed by the new palladium complexes.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	[Pd] (mol-%)	T [°C]	t [h]	Conversion (%)[b]	Yield (%)[c]
1	**4**	4-bromoacetophenone	Cs_2CO_3	DMF	1	135	1.5	92	86
2	**5**	4-bromoacetophenone	KF	DMA	1	135	1.5	84	–
3	**6**	4-bromoacetophenone	K_3PO_4	DMA	1	135	1.5	80	–
4	**7**	4-bromoacetophenone	KF	DMA	1	135	1.5	89	–
5	**4**	methyl 4-bromobenzoate	Cs_2CO_3	DMF	1	135	1.5	95	90
6	**4**	4-bromotoluene	Cs_2CO_3	DMF	1	135	6	99	87
7	**4**	4-bromoanisole	Cs_2CO_3	DMF	1	135	12	96	91
8	**4**	4-bromoacetophenone	Cs_2CO_3	DMF	0.1	135	6	81	75
9	**4**	4-bromoacetophenone	Cs_2CO_3	DMF	0.001	135	24	21	–
10	**4**	4-chloroacetophenone	Cs_2CO_3	DMF	3	135	48	57	–
11	**4**	4-chloroanisole	Cs_2CO_3	DMF	5	135	48	56	–

[a] Reaction conditions: 1.0 mmol aryl halide, 1.3 mmol styrene, 1.5 mmol base, 2 mL solvent. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yield (average of two experiments).

Experimental Section

General Procedure: All manipulations were carried out under nitrogen using standard Schlenk-line or drybox techniques. Solvents (THF, toluene, CH_2Cl_2 and hexane) were refluxed over an appropriate drying agent and distilled prior to use. Methanol (Merck, 99.9%), DMA (TEDIA, 99%) and DMF (TEDIA, 95%) were used as supplied. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian Gemini-200 (200 MHz), Varian Mercury-400 (400 MHz) and Varian Inova-600 (600 MHz) spectrometers. Spectra were recorded in chloroform-*d* at ambient temperature unless otherwise stated, and referenced internally to the residual solvent peak, and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed with an Elementar Vario ELIV instrument.

Chemicals were used as supplied unless otherwise stated. NEt_3 was dried with CaH_2 and distilled before use. 2,2-Dimethyl-*N*,*N*′-diphenyl-malonamide and 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride were prepared by a method reported in the literature.[31]

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=N(CH$_2$)$_2$Cl(C^A–N^B)(C^B–C^C) (1): To a flask containing 2,2-dimethyl-*N*,*N*′-diphenylpropanediimidoyl dichloride (2.5 g, 8.0 mmol) and NEt_3 (4.5 mL, 32 mmol), 40 mL CH_2Cl_2, 2-chloroethylamine hydrochloride (2.8 g, 24 mmol) was added at 0 °C. The reaction mixture was warmed to room temperature and left to react overnight. After 14 h of stirring, the volatiles were removed in vacuo, and the residue was extracted with 30 mL toluene. After removal of solvent, the residue was washed with 5 mL hexane to afford a white solid. Yield, 1.84 g, 70.5%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.46 [s, 6 H, $C(CH_3)_2$], 3.74 [m, 4 H, $(CH_2)_2$], 6.94 (d, ^3J = 7.2 Hz, 2 H, *o*-Ph), 7.08 (t, ^3J = 7.8 Hz, 1 H, *p*-Ph), 7.16 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.30 (t, ^3J = 7.8 Hz, 2 H, *m*-Ph), 7.39 (t, ^3J = 7.8 Hz, 2 H, *m*-Ph), 8.27 ppm (d, ^3J = 7.8 Hz, 2 H, *o*-Ph). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 21.7 [s, $C(CH_3)_2$], 45.0 [s, $(CH_2)_2$], 50.4 [s, $(CH_2)_2$], 58.0 [s, *tert*-$C(CH_3)_2$], 119.4, 121.4, 123.4, 124.6, 128.7 (overlap) (*o*, *m*, *p*-C_6H_5), 137.1, 146.7, 157.8, 159.6 ppm (two C_{ipso}-C_6H_5 and two *C*=*N* groups). $C_{19}H_{20}N_3Cl$ (325.84): calcd. C 70.04, H 6.19, N 12.90; found C 69.88, H 6.28, N 12.74.

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=N(CH$_2$)$_2$S(CMe$_3$)(C^A–N^B)(C^B–C^C) (2): To a flask containing **1** (0.49 g, 1.5 mmol) and K_2CO_3 (0.62 g, 4.5 mmol), 40 mL DMF, 2-methyl-2-propanethiol (0.34 mL, 3.0 mmol) was added. The reaction mixture was heated to 70 °C and left to react overnight. After 16 h of stirring, the resulting suspension was cooled to room temperature. Water (ca. 30 mL) was added into the suspension, which was then put into the fridge, and subsequently afforded a white solid. Yield, 0.49 g, 85.4%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.35 [s, 9 H, $C(CH_3)_3$], 1.45 [s, 6 H, $C(CH_3)_2$], 2.80 (t, ^3J = 7.2 Hz, 2 H, CH_2), 3.57 (t, ^3J = 7.8 Hz, 2 H, CH_2), 6.93 (d, ^3J = 7.2 Hz, 2 H, *o*-Ph), 7.07 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.14 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.28 (t, ^3J = 7.8 Hz, 2 H, *m*-Ph), 7.38 (t, ^3J = 7.8 Hz, 2 H, *m*-Ph), 8.27 ppm (d, ^3J = 7.8 Hz, 2 H, *o*-Ph). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 21.7 [s, $C(CH_3)_2$], 30.2 (s, CH_2), 31.0 [s, $C(CH_3)_3$], 42.2 [s, $C(CH_3)_3$], 49.1 (s, CH_2), 58.0 [s, $C(CH_3)_2$], 119.4, 121.5, 123.3, 124.4, 128.6 (overlap) (CH-C_6H_5), 137.2, 146.8, 158.0, 158.4 ppm (two C_{ipso}-C_6H_5, and two *C*=*N* groups). $C_{23}H_{29}N_3S$ (379.56): calcd. C 72.78, H 7.70, N 11.07; found C 72.35, H 7.30, N 11.01.

PhN=C^A(C^{B}Me$_2$)(N^{B}Ph)C^C=N(CH$_2$)$_2$SPh(C^A–N^B)(C^B–C^C) (3): The procedure for the preparation of **3** was similar to that used for **2**. A white solid was obtained. Yield, 0.46 g, 91.0%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.34 [s, 6 H, $C(CH_3)_2$], 3.19 (t, ^3J = 7.2 Hz, 2 H, CH_2), 3.63 (t, ^3J = 7.2 Hz, 2 H, CH_2), 6.91 (d, ^3J = 7.2 Hz, 2 H, *o*-Ph), 7.06 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.14 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.16 (t, ^3J = 7.2 Hz, 1 H, *p*-Ph), 7.26 (m, overlap, 4 H, Ph), 7.37 (m, overlap, 4 H, Ph), 8.24 ppm (d, ^3J = 7.8 Hz, 2 H, *o*-Ph). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 21.5 [s, $C(CH_3)_2$], 35.2 (s, CH_2), 48.3 (s, CH_2), 58.0 [s, $C(CH_3)_2$], 119.4, 121.4, 123.3, 124.5, 126.1, 128.6 (overlap), 128.9, 129.3 (CH-C_6H_5), 136.1, 137.1, 146.7, 157.9, 168.8 ppm (three C_{ipso}-C_6H_5, and two *C*=*N* groups). $C_{25}H_{25}N_3S$ (399.55): calcd. C 75.15, H 6.31, N 10.52; found C 75.31, H 6.09, N 10.55.

[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$S(CMe$_3$)(C^A–N^B)-(C^B–C^C)]Pd(OAc) (4): To a flask containing $Pd(OAc)_2$ (0.11 g, 0.50 mmol) and **2** (0.19 g, 0.50 mmol), 30 mL THF was added at room temperature. After 12 h of stirring, the yellow suspension was filtered and the filtrate was dried in vacuo to afford a pale brown solid. Yield, 0.22 g, 79.2%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.47 [s, 6 H, $C(CH_3)_2$], 1.58 [s, 9 H, $C(CH_3)_3$], 2.16 [s, 3 H, O-C(=O)-CH_3], 2.71 (t, ^3J = 6.0 Hz, 2 H, CH_2), 3.76 (t, ^3J = 6.0 Hz, 2 H, CH_2), 6.94 (d, ^3J = 7.2 Hz, 2 H, *o*-Ph), 7.06 (t, ^3J = 7.2 Hz, 1 H, *CH*-Ph), 7.13 (t, ^3J = 7.2 Hz, 1 H, *CH*-Ph), 7.17 (t, ^3J = 7.2 Hz, 1 H, *CH*-Ph), 7.33 (t, ^3J = 7.8 Hz, 2 H, *m*-Ph), 7.59 (d, ^3J = 8.4 Hz, 1 H, *CH*-Ph), 8.09 ppm (d, ^3J = 7.8 Hz, 1 H, *CH*-Ph). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 21.0 [s, $C(CH_3)_2$], 24.6 [s, O-C(=O)-CH_3], 30.0 [s, $C(CH_3)_3$], 30.7 (s, CH_2), 48.6 [s, $C(CH_3)_3$], 52.6 (s, CH_2), 57.0 [s, $C(CH_3)_2$], 116.6, 120.8, 124.1, 124.8, 125.5, 129.0, 134.1 (CH-C_6H_5), 129.6, 129.9, 145.5, 153.2, 158.7 (one η^1-Ph, two C_{ipso}-C_6H_5 and two *C*=*N* groups), 177.6 ppm [s, O-*C*(=O)-CH_3]. $C_{25}H_{31}N_3O_2PdS$ (544.02): calcd. C 55.19, H 5.74, N 7.72; found C 54.72, H 5.99, N 7.34.

[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$SPh(C^A–N^B)(C^B–C^C)]Pd(OAc) (5): The procedure for the preparation of **5** was similar to that used for **4**; however, compound **3** was used instead of **2**. A pale brown solid was obtained. Yield, 0.18 g, 61.9%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.44 [s, 6 H, $C(CH_3)_2$], 2.08 [s, 3 H, OC(O) CH_3], 2.98 (t, ^3J = 6.0 Hz, 2 H, CH_2), 3.65 (t, ^3J = 6.0 Hz, 2 H, CH_2), 6.93 (m, 2 H, *CH*-Ph), 7.11 (m, 1 H, *CH*-Ph), 7.13 (m, 1 H, *CH*-Ph), 7.21 (m, 1 H, *CH*-Ph), 7.33 (m, 2 H, *CH*-Ph), 7.43 (m, 3 H, *CH*-Ph), 7.78 (m, 1 H, *CH*-Ph), 8.13 ppm (m, 3 H, *CH*-Ph). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 21.0 [s, $C(CH_3)_2$], 24.0 [s, O-C(=O)-CH_3], 39.2 (s, CH_2), 52.1 (s, CH_2), 57.1 [s, $C(CH_3)_2$], 116.7, 120.8, 124.2, 124.9, 125.8, 129.0, 129.6, 129.7, 133.5, 134.4 (CH-C_6H_5), 129.76, 129.82, 129.87, 145.5, 153.2, 158.8 (one η^1-Ph, three C_{ipso}-C_6H_5 and two *C*=*N* groups), 177.3 ppm [s, O-*C*(=O)-CH_3]. $C_{27}H_{27}O_2N_3PdS$ (564.01): calcd. C 57.50, H 4.83, N 7.45; found C 57.26, H 5.08, N 7.36.

[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$S(CMe$_3$)(C^A–N^B)-(C^B–C^C)]PdCl (6): To a flask containing **4** (0.14 g, 0.25 mmol) and LiCl (0.04 g, 1.0 mmol) 30 mL methanol was added at room temperature. After 0.5 h of stirring, the yellow suspension was filtered and the precipitate was washed with 20 mL deionized water followed by 20 mL hexane to afford a yellow solid. Yield, 0.068 g, 52.4%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.50 [s, 6 H, $C(CH_3)_2$], 1.66 [s, 9 H, $C(CH_3)_3$], 2.71 (t, ^3J = 6.6 Hz, 2 H, CH_2), 3.79 (t, ^3J = 6.6 Hz, 2 H, CH_2), 6.95 (m, 2 H, *CH*-Ph), 7.07 (t, ^3J = 6.6 Hz, 1 H, *CH*-Ph), 7.14 (t, ^3J = 7.2 Hz, 1 H, *CH*-Ph), 7.16 (t, ^3J = 7.2 Hz, 1 H, *CH*-Ph), 7.34 (t, ^3J = 7.8 Hz, 1 H, *CH*-Ph), 8.10 (d, ^3J = 7.8 Hz, 1 H, *CH*-Ph), 8.41 ppm (d, ^3J = 7.8 Hz, 1 H, *CH*-Ph). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 21.1 [s, $C(CH_3)_2$], 30.6 [s, $C(CH_3)_3$], 31.3 (s, CH_2), 49.9 [s, $C(CH_3)_3$], 53.1 (s, CH_2), 57.0 [s, $C(CH_3)_2$], 116.8, 120.8, 124.2, 125.1, 125.5, 129.0, 138.9 (CH-C_6H_5), 130.1, 130.2, 145.5, 153.1, 158.7 ppm (one η^1-Ph, two C_{ipso}-C_6H_5, and two *C*=*N* groups). $C_{23}H_{28}ClN_3PdS$ (520.43): calcd. C 53.08, H 5.42, N 8.07; found C 53.29, H 5.36, N 8.40.

[PhN=C^A(C^{B}Me$_2$)(N^B-η^1-C$_6$H$_4$)C^C=N(CH$_2$)$_2$SPh(*C*^{A}–*N*^{B})(*C*^{B}–*C*^{C})]PdCl (7): The procedure for the preparation of **7** was similar to that used for **6**; however, compound **5** was used instead of **4**.A yellow solid was obtained. Yield, 0.274 g, 87.0%. ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ = 1.46 [s, 6 H, C(C*H*$_3$)$_2$], 2.99 (t, ^3J = 6.0 Hz, 2 H, C*H*$_2$), 3.76 (br., 2 H, C*H*$_2$), 6.97 (d, ^3J = 7.2 Hz, 2 H, *o*-Ph), 7.04 (m, 1 H, C*H*-Ph), 7.14 (t, ^3J = 7.2 Hz, 1 H, C*H*-Ph), 7.19 (t, ^3J = 7.2 Hz, 1 H, C*H*-Ph), 7.35 (t, ^3J = 7.8 Hz, 2 H, *m*-Ph), 7.47 (m, 3 H, C*H*-Ph), 8.11 (m, 2 H, C*H*-Ph), 8.17 (d, ^3J = 8.4 Hz, 1 H, C*H*-Ph), 8.40 ppm (m, 1 H, C*H*-Ph). ^{13}C{^{1}H} NMR (150 MHz, CD$_2$Cl$_2$): δ = 21.0 [s, C(*C*H$_3$)$_2$], 39.2 (s, *C*H$_2$), 53.3 (s, *C*H$_2$), 57.4 [s, *C*(CH$_3$)$_2$], 117.1, 120.9, 124.3, 124.7, 125.7, 129.2, 129.8, 130.0, 133.4, 138.9 (*C*H-*C*$_6$H$_5$), 129.6, 130.3, 130.7, 145.8, 153.7, 159.0 ppm (one η^1-Ph, three *C*$_{ipso}$-*C*$_6$H$_5$, and two *C*=*N* groups). $C_{25}H_{24}ClN_3PdS$ (540.42): calcd. C 55.56, H 4.48, N 7.78; found C 55.47, H 4.070, N 7.80.

General Procedure for the Suzuki-Type Coupling Reaction: Prescribed amounts of catalyst, base (2.0 equiv.), boronic acid (1.5 equiv.), and aryl halide (1.0 equiv.) were placed under nitrogen in a Schlenk tube. Solvent (2 mL) was added by syringe, and the reaction mixture was heated at the prescribed temperature for the prescribed amount of time.

General Procedure for the Heck Reaction: Prescribed amount of catalysts, base (1.5 equiv.) and aryl halide (1 equiv.) were placed under nitrogen in a Schlenk tube. Solvent (2 mL) and styrene (1.3 equiv.) were added by syringe, and the reaction mixture was heated at the prescribed temperature for the prescribed amount of time.

Crystal Structure Data: Crystals were grown from CHCl$_3$ solution (**3**) or a CH$_2$Cl$_2$/hexane solution (**4**), and then isolated by filtration. Suitable crystals of **3** or **4** were sealed in thin walled glass capillaries under nitrogen and mounted on a Bruker AXS SMART 1000 diffractometer. Absorption corrections were based on symmetry equivalent reflections and applied using the SADABS program. Space group determinations were based on the Laue symmetries and systematic absences exhibited by the diffraction patterns, and were confirmed by the structure solutions. The structures were solved by direct methods using the SHELXTL package. All non-hydrogen atoms were located from successive difference Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms, and fixed isotropic parameters were used for the hydrogen atoms. The asymmetric unit of **4** contains a severely disordered molecule of dichloromethane, and a molecule of water. Crystallographic data collection and refinement details are given in Table 5.

Table 5. Summary of crystal data for compounds **3** and **4**.

	3	**4**
Formula	$C_{25}H_{25}N_3S$	$C_{26}H_{35}Cl_2N_3O_3PdS$
Fw	399.54	646.93
T [K]	293(2)	293(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	7.9986(8)	22.7849(14)
b [Å]	11.6307(11)	13.2886(8)
c [Å]	12.1069(11)	20.8977(13)
α [°]	90.187(2)	90
β [°]	98.050(2)	112.7370(10)
γ [°]	100.699(2)	90
V [Å^3]	1095.32(18)	5835.7(6)
Z	2	8
ρ_{calc} [Mg/m^3]	1.211	1.473
μ(Mo-K_α) [mm^{-1}]	0.163	0.922
Reflections collected	6263	16054
No. of parameters	262	335
$R1$[a]	0.0491	0.0422
$wR2$[a]	0.1452	0.1332
GoF[b]	1.065	1.14

[a] $R1 = [\Sigma(|F_o| - |F_c|)/\Sigma |F_o|]$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 0.10$. [b] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{\text{rflns}} - N_{\text{params}})]^{1/2}$.

CCDC-269677 and -269678 for compounds **3** and **4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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